Fate of bromine in pyrolysis of printed circuit board wastes

Yi-Chi Chien\textsuperscript{a}, H. Paul Wang\textsuperscript{a,\textasteriskcommand}{*}, Kuen-Song Lin\textsuperscript{a}, Y.-J. Huang\textsuperscript{a}, Y.W. Yang\textsuperscript{b}

\textsuperscript{a} Department of Environmental Engineering, Cheng Kung University, Tainan, Taiwan, ROC
\textsuperscript{b} Synchrotron Radiation Research Center, Hsinchu, Taiwan, ROC

Received 30 March 1999; accepted 5 June 1999

Abstract

Behavior of Br in pyrolysis of the printed circuit board waste with valuable copper and oil recycling has been studied in the present work. Experimentally, pyrolysis of the printed circuit board waste generated approximately 40.6\% of oils, 24.9\% of noncondensible gases and 34.5\% of solid residues that enriched in copper (90–95\%). The cuts of the oils produced from pyrolysis of the printed circuit board waste into weighted boiling fraction were primarily light naphtha and heavy gas oil. Approximately 72.3\% of total Br in the printed circuit board waste were found in product gas mainly as H\textsubscript{2}Br and bromobenzene. However, by extended X-ray absorption fine structural (EXAFS) spectroscopy, Cu–O and Cu–(O)–Cu species with bond distance of 1.87 and 2.95 Å, respectively, were observed in the solid residues. Essentially, no Cu–Br species was found. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Pyrolysis; Printed circuit board; Recycling; EXAFS; Bromine

1. Introduction

Over 100,000 TPY (tons per year) of printed circuit board wastes are disposed off in Taiwan. Due to a high bromine content, printed circuit board wastes are very difficult to be treated effectively. Many techniques such as landfill, incineration and low-level reutilization or recycling have been used in disposal of printed circuit board wastes (Miyazaki et al., 1995; Sum, 1991; Bueken and Schoeters, 1986). Incineration of printed circuit board wastes does not count towards meeting the EU minimum recycling target of 15\%. In addition, the 5–15\% of Br in printed circuit board wastes may cause an operational difficulty in handling of incineration byproducts such as H\textsubscript{2}Br, Br\textsubscript{2} and toxic brominated polycyclic aromatic hydrocarbons (PAHs) and dioxin (Mattila et al., 1992). At present, only solidification/landfilling of printed circuit board wastes is practised on a large scale, however, its cost is rising rapidly and the acceptance of this method is decreasing.

Pyrolysis has been recognized as an effective resource recovery alternative. Pyrolysis of wastes has been investigated in vacuum, molten salt, fluidized bed, rotary kiln, entrained, stationary and moving bed reactors (Williams et al., 1990). Recently, recovery of olefins and other hydrocarbons by pyrolysis of plastic and rubber wastes has been demonstrated in a pilot-scale fluidized-bed reactor (Williams et al., 1990; Poller, 1980).

The main constituent in printed circuit board wastes is resin that is produced originally from crude oil and can be thermally cracked into fuels or petrochemicals (Castagnoli et al., 1994). Printed circuit board wastes also represent a significant quantity of energy in terms of the energy consumed in processing petroleum. Recover part of this energy content in a form with the highest possible value, i.e., fuel oil, would be economically and environmentally attractive (Castagnoli et al., 1994). However, there is a limited Br content in product oil and emissions. Thus, the main objective of the present work was to investigate the fate of Br in pyrolysis of printed...
circuit board wastes. Characteristics of product oils or gases were determined by FTIR and proton NMR spectroscopic methods (Qian and Zhang, 1984; Srica et al., 1993). Fine structural properties of copper in the solid residue in the pyrolysis process were also studied by X-ray absorption spectroscopy.

2. Experimental

Pyrolysis of the printed circuit board wastes was carried out in a fixed-bed reactor at 623–1073 K for 30 min in high purity nitrogen (>99.9%) with a gas hourly space velocity (GHSV) of 1000 h\(^{-1}\). Pyrolysis product gases were passed through a water cooler and analyzed by on-line FTIR spectroscopy (Bio-Rad FTS-40 (10-cm gas cell)). The noncondensible gases were scrubbed with a 1 M NaOH solution before being emitted. Product oils were separated and collected in knockout drums.

Elemental analyses of the printed circuit board wastes were determined by an elementary analyzer (EA, Heraeus). Chemical and fuel characteristics of product oils were investigated using analytical techniques such as simulate distillation (Perkin Elmer 5000-GC/FID, ASTM D2887 method) and proton NMR (proton nuclear magnetic resonance, Bruker AMX 400 FT-NMR) and FTIR spectroscopies. Infrared spectra were recorded on a Digilab FTIR spectrometer (Bio-Rad FTS-40) with fully computerized data storage and data handling capability. For all spectra reported, a 64-scan data accumulation was conducted at a resolution of 4 cm\(^{-1}\). Concentrations of Br and Cu in the samples were measured by ICP-MS (LEAN, Model 5000).

Pyrolysis of printed circuit board wastes was also conducted in a thermal gravimetric analyzer (SDT 2960 and Thermal Analyst 2000, TA Instrument) with a capability of determining weight loss and temperature difference simultaneously. Temperature and sample weight were recorded at 10 s intervals. About 10 mg of the printed circuit board waste sample was heated from 303 to 1073 K at a heating rate of 5 K min\(^{-1}\) with a sensitivity of 0.1 \(\pm\) 0.01\(\mu\)g in flowing high purity nitrogen (100 ml min\(^{-1}\)). In all TGA experiments, aluminum oxide was used as a reference.

The EXAFS spectra were collected at beamline B-11B at the Taiwan Synchrotron Radiation Research Center. The B-11B has a bending-magnet double-crystal monochromator (DCM) X-ray beamline which provides highly monochromatized photon beams with energies from 1 to 9 keV and resolving power \((E/\Delta E)\) of up to 7000. Data were collected in fluorescence detection mode with a Lytle detector in the region of the Cu K edge (8979 eV) at 298 K. The absorption spectra were collected in ion chambers that were filled with helium gas. The photon energy was calibrated at the Cu K-edge by recording spectrum of copper foil. The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 7.0 programs (Stern et al., 1995).

3. Results and discussion

Analysis of the typical printed circuit board waste powder is shown in Table 1. Note that the printed circuit board waste contained 8.38 wt% of Br and 9.53 wt% of Cu. Pyrolysis of the printed circuit board waste was conducted in the thermal gravimetric analyzer (TGA) and in the fixed-bed reaction system. Effect of pyrolysis temperature on the conversion of the printed circuit board waste is shown in Fig. 1(a). It is apparent that the pyrolytic conversion in the TGA is similar to that in the fixed-bed reactor at 623–723 K. However, at higher temperatures (723–1073 K), due to a diffusion limitation in the resin matrix, an increase in the pyrolysis temperature may not enhance the conversion in pyrolysis of the printed circuit board waste. The maximum conversion was limited to 70–80% at 723–1073 K. As shown in Fig. 2, pyrolysis of the printed circuit board waste at

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Main constituents (wt%) of the typical printed circuit board waste powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>52.21</td>
</tr>
<tr>
<td>H</td>
<td>6.11</td>
</tr>
<tr>
<td>O</td>
<td>Balanced</td>
</tr>
<tr>
<td>N</td>
<td>2.56</td>
</tr>
<tr>
<td>Br</td>
<td>8.53</td>
</tr>
<tr>
<td>S</td>
<td>Trace</td>
</tr>
<tr>
<td>Cl</td>
<td>Trace</td>
</tr>
<tr>
<td>Cu</td>
<td>9.53</td>
</tr>
<tr>
<td>Moisture</td>
<td>3.50</td>
</tr>
</tbody>
</table>

Fig. 1. Effect of temperature on the conversion for pyrolysis of the printed circuit board waste: (a) in the fixed-bed reactor with a GHSV of 1000 h\(^{-1}\) and (b) in the TGA.
higher temperatures may increase the productivity of gas and oil at the expense of solid residues. Pyrolysis of printed circuit board wastes at 823 K for 30 min generated approximately 40.6 wt% of oils, 24.9 wt% of gases and 34.5 wt% of solid residue.

Fig. 3 shows that aliphatics (bands with an intense infrared absorbance at 2800–3000 (stretching) and 1375–1450 cm\(^{-1}\) (bending)) are the major constituent in the product oils. In addition, bromobenzene was also observed (bands with an intense infrared absorbance at 755 cm\(^{-1}\)) in the product oils. Note that the oil contained about 1.3% of Br. Proton NMR data show that the oils contain approximately 93.2% of aliphatics and 6.8% of aromatics (see in the corner of Fig. 3). The side chain carbon number in product oil was two. The NMR data are also suggestive of the occurrence of cyclization in pyrolysis of the printed circuit board waste since the aromatic content in product oil increased.

The cuts of the produced oils from the printed circuit board wastes pyrolysis into weighted boiling fraction were distinguished: light naphtha 3.94%, heavy naphtha 18.17%, light gas oil 45.90%, and heavy gas oil 31.98%. Naphtha and light gas oil are the main constituents of gasoline and diesel, respectively. Heavy gas oil may be re-refined into lighter products or sold as a low-grade fuel oil. The composition of gases produced from the pyrolysis of printed circuit board wastes was also studied by in situ FTIR spectroscopy. The bromobenzene was also found in the gaseous product. As shown in the right corner of Fig. 4, bromobenzene is observed spectroscopically in pyrolysis of the wastes at 623–823 K. It should be noted that only 5.1% of Br was found in the solid residues. Approximately 72.3% of Br may be emitted in the off-gas stream. Fig. 4 shows that in addition to bromobenzene, HBr was also found in the off-gas.

Effect of the pyrolysis temperature and residence time on the infrared absorbance of HBr formed in the pyrolysis of printed circuit board wastes is showed in Fig. 5. It is clearly seen that the HBr with an appreciable absorbance is observed at temperatures greater than 373 K. An increase in the pyrolysis temperature leads to an absorbance increasing for the HBr band at 373–773 K. At 873 K, an increase in pyrolysis time does not change significantly the absorbance of the HBr band.

The extended X-ray absorption fine structural (EXAFS) spectrum of copper species in residues of pyrolysis of the printed circuit board wastes is shown in Fig. 6. An over 99% reliability of EXAFS data fitting (dotted line) for the copper species was observed. It is clear that oxygen and copper were the major atoms coordinated to the central Cu atom in the pyrolysis residue. Table 2 also shows the structure parameters obtained from the best fit to the EXAFS data. The bond distance of Cu–O was 1.87 Å with a coordination number (CN) of 2.3. In all EXAFS data analyses, the Debye–Waller factors (\(\Delta r^2\)) were less than 0.01 (\(\Delta r < 0.1 \text{ Å in general}\)). It should be noted that Cu–Br species (bond distance of 2.95 Å) in the residues of pyrolysis of printed circuit board wastes was not found. Thus, one may eliminate the possibility that Br interacted with copper in pyrolysis of the printed circuit board wastes.
4. Conclusions

Fate of Br in pyrolysis of printed circuit board wastes with product oil recycling has been investigated. Experimentally, pyrolysis of the printed circuit board wastes at 823 K for 30 min generated approximately 40.6% of oils, 24.9% of noncondensible gases and 34.5% of solid residues. The cuts of the oils produced from the printed circuit board wastes pyrolysis into weighted boiling fraction are primarily light naphtha and heavy gas oil. Most Br species, mainly bromobenzene and HBr, were found in the o/C128-gas stream. Bromobenzene was also found in product oils. Since the EXAFS data do not suggest an existence of Cu–Br bonding in the solid residue, one may eliminate the possibility that Br interacted with copper in the pyrolysis of the printed circuit board wastes.

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>CN</th>
<th>Bond distance (Å)</th>
<th>Δσ² (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu–O</td>
<td>2.46</td>
<td>1.87</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>2.11</td>
<td>3.58</td>
<td>0.009</td>
</tr>
<tr>
<td>Cu–(O)–Cu</td>
<td>4.24</td>
<td>2.79</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>5.67</td>
<td>4.53</td>
<td>0.009</td>
</tr>
</tbody>
</table>

CN: Coordination number; σ: Debye–Waller factor.

Fig. 4. Infrared spectra of product gases generated from pyrolysis of the printed circuit board waste at 823 K for 30 min. In the right corner, development of the IR band for bromobenzene at: (a) 293 K; (b) 373 K; (c) 473 K; (d) 623 K; (e) 773 K and 823 K for (f) 10 min; (g) 8 min; (h) 6 min; (i) 4 min and (j) 2 min.

Fig. 5. Infrared spectra of product gases generated from pyrolysis of the printed circuit board waste at: (a) 293 K; (b) 373 K; (c) 473 K; (d) 623 K; (e) 773 K and 823 K for (f) 10 min; (g) 8 min; (h) 6 min; (i) 4 min and (j) 2 min.

Fig. 6. Fourier transform (FT) of the Cu K-edge EXAFS spectra of the solid residues generated from pyrolysis of the printed circuit board waste. The experimental data are the solid line and the best fit is expressed by the dotted line.

Table 2

Structural parameters for residues of pyrolysis of the printed circuit board wastes

4. Conclusions

Fate of Br in pyrolysis of printed circuit board wastes with product oil recycling has been investigated. Experimentally, pyrolysis of the printed circuit board wastes at 823 K for 30 min generated approximately 40.6% of oils, 24.9% of noncondensable gases and 34.5% of solid residues. The cuts of the oils produced from the printed circuit board wastes pyrolysis into weighted boiling fraction are primarily light naphtha and heavy gas oil. Most Br species, mainly bromobenzene and HBr, were found in the off-gas stream. Bromobenzene was also found in product oils. Since the EXAFS data do not suggest an existence of Cu–Br bonding in the solid residue, one may eliminate the possibility that Br interacted with copper in the pyrolysis of the printed circuit board wastes.
Acknowledgements

The financial support of the National Science Council, Taiwan, ROC. (NSC-84-2211-E-006-022, NSC-85-2621-P-006-003, and NSC-86-2113-M-006-020) and CALEC Co. (83-S78) is gratefully acknowledged by the authors.

References


